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**Structural evolution during calcination and sintering of a
(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-δ} nanofiber prepared by electrospinning**

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Abstract

Design of 3-dimensional metal oxide nanofibers by electrospinning is being widely explored. However, the impacts of calcination and sintering on the resulting morphology remain unknown. For the first time, (La_{0.6}Sr_{0.4})_{0.99}CoO_{3-δ} (LSC) nanofiber, which is among the most promising electrode materials for solid oxide fuel cells, was synthesized by sol-gel electrospinning. By elevating the temperature in oxygen using in situ transmission electron microscopy, we discovered the structural transitions from nanofibers to nanotubes and then to nano-pearl strings. This facile and up-scalable method can be widely applied to design metal oxide one-dimensional nanomaterials with precise control in both geometry (nanofiber, nanotube and nano-pearl string) and surface area (by varying grain size).

1. Introduction

Nanofibers are one-dimensional (1D) nanomaterials that have unique physicochemical properties such as high surface area, high strength, high electronic/ionic conductivity and 1-dimensionality. One of important applications is catalysis, where 1D materials of carbon [1] or metal oxides [2] have been synthesized to replace conventional catalyst systems and increase the catalytic performance. The performance and commercialization of such 1D materials strongly depend on further development of synthesis methods that allow for the control of both composition and structure while still being cost-effective and up-scalable.

Electrospinning is an efficient and cost-effective method to produce 1D materials [3-5]. Combined with sol-gel chemistry and calcination, electrospinning has been used to produce a variety of 1D metal oxide nanomaterials that bring remarkable performance enhancement in energy devices (e.g. lithium ion batteries [6, 7], solid oxide fuel cells [8-10]). Moreover, by using co-axial spinnerets or by adjusting calcination parameters, nanofibers can be transformed into nanotubes [11], nano-pearl-strings [12] or nanobelts [13]. These 1D materials with hierarchical structure provide exceptionally high surface-to-volume ratio, facile strain relaxation and improvement in electrochemical performance. In particular, the catalysts with 1D nanotube structures has attracted much attention, owing to the shorter diffusion lengths, higher electronic conductivity and higher surface area [6, 14].

For example, nano-pearl-string TiNb_2O_7 nanofibers were fabricated by annealing electrospun nanofibers (containing precursors and polymer binders) at 1000°C in air for 10 h [12]. As anode material for lithium batteries, this material shows efficient 1D electron transport along longitudinal direction, improved connectivity with electronic and ionic sources and short diffusion distance. TiO_2 hollow nanofibers were synthesized by electrospinning using a dual nozzle, where a solution containing PVP and titanium isopropoxide was filled in the outer layer of the nozzle with its inner core filled by mineral oil. After calcination, the resulting nanofibers with the hollow geometry showed twice higher rate capability compared to that of pristine TiO_2 nanofiber at 5°C due to shorter diffusion distance of lithium ion and higher lithium ion flux [11]. However, electrospinning with dual nozzle is complicated and difficult to be scaled up for industrial production. Therefore, a simple, precise and up-scalable process is required to design hierarchical structures of nanofibers and enhance their performance in energy devices.

A conventional method of producing metal oxide ceramic nanofibers involves three steps: 1) mixing precursors, carrier polymer and solvent; 2) electrospinning the mixture into polymeric nanofiber membrane; 3) converting the polymeric nanofibers to metal oxide nanofibers by calcination and sintering. The major purpose of the third step is often considered to be the decomposition of precursors and removal of polymers. Convention electron microscopy is often used to offer valuable insight into the 1D structure before and after calcination and sintering, but such post mortem of analysis does not allow one to follow the structural evolution of the nanofibers. The structural evolution of electrospun metal oxide 1D materials during calcination and sintering is therefore generally unknown.

In situ transmission electron microscopy (in situ TEM) is a method that allows for direct imaging of nano-materials during chemical reactions with nanoscale resolution and has been used to describe nanostructural dynamics [15-21]. In the present work, we use in situ TEM to reveal the structural evolution of an electrospun $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_{3.5}$ (LSC) nanofiber while it was calcined and sintered in oxygen. Complementary to the structural analysis, thermogravimetric analysis (TGA) is used to obtain

insight in the chemical reactions as a function of temperature. LSC is chosen in this study because this perovskite has been intensively studied for electrochemical devices, e.g. solid oxide fuel cells [22].

2. Experimental

2.1 Electrospinning

La(NO₃)₃·6H₂O, Sr(NO₃)₂ and Co(NO₃)₃·6H₂O were dissolved in deionized H₂O at a molar ratio of 0.6:0.4:1 in order to synthesis (La_{0.6}Sr_{0.4})_{0.99}CoO_{3-δ} (LSC). The solution was stirred at 60°C until complete dissolution. Polyvinylpyrrolidone (PVP) with an average molecular weight of 1,300,000 was used as carrier polymer in this experiment. A desired amount of PVP powder was added to the above solution. In this case, the mass ratio of PVP powder to nitrate salts was set as 0.4. Higher ratios of PVP over nitrate salt resulted in finer LSC nanofibers. Lower ratios of PVP resulted in electrosprayed droplets instead of nanofibers. The solution was stirred at 60 °C until a clear pink solution was formed. The mixture was then loaded into a 10 ml syringe with a 21 gauge stainless steel needle attached to the tip of the syringe. The syringe was then mounted on a syringe pump. During electrospinning, the mixture was pumped out of the needle at an injection rate of 0.3 ml/h with an electrical field of 4.4 kV/cm. A grounded aluminum (Al) foil was used as the collector to collect the electrospun nanofibers.

2.2 In situ TEM

The in situ TEM experiments were performed using a Titan 80-300 (FEI) electron microscope equipped with a differentially pumped environmental cell [23] operated at 300 keV. Heating was facilitated by an Aduro 300 heating holder (Protochips Inc.) which is a chip based heating holder. The as-spun nanofiber membrane was peeled off from the Al collector foil and deposited on a thermal chip (Protochips Inc.) by adding a droplet of the electrospun nanofibers suspended in acetone to the surface of the chip and allowing the acetone to evaporate in air at room temperature. The chips used for the experiments were so-called “no-carbon” type, which means that the sample is supported directly by the ceramic heating membrane of the chip. The in situ experiment was performed by exposing the sample to 2 mbar O₂ (AGA 6.0) while constantly ramping the temperature by 5°C/min and recording time-lapsed TEM images and diffraction patterns of the same fiber. Image analysis is performed using the software ImageJ. The fiber diameters were measured by drawing a straight line from edge to edge across the fiber. The diameters of nanograins were measured by outlining the grains using the Polygon selection tool and calculating a diameter from the measured area by assuming a circular geometry. Line intensity profiles across the fiber were acquired by using the Plot profile tool. The line profiles were averaged along the length of the fiber. Crystal lattice distances measured in selected area electron diffraction (SAED) pattern were compared with crystallographic data from the ICSD database.

2.2.1 Temperature calibration

Since the commercial thermal chips were calibrated by the company only in vacuum, it is necessary to calibrate the temperatures for the in situ experiment in the relevant gas at the relevant pressure. The calibration is here based on a comparison of two oxidation experiments of carbon black super 65 (Timcal) in 2 mbar O₂ with a constant temperature ramping rate of 10°C/min, by using the TEM holder from Protochips and a TEM heating holder from DENSsolutions. The later heating holder provides the temperature feedback based on a 4-point-probe resistive measurement of the micro hotplate, which is assumed to be reliable under the present conditions. The relative motion and shrinkage of the carbon black were measured in the two experiments. Based on the comparison of the two results, we found that the set temperature of the Protochips holder was consistent with the measured temperature from the DENSsolutions holder within 10 °C.

2.2.2 Electron beam effects

From the TEM images, the LSC particle sizes were measured by using a circular approximation to their projected area. All measurements were performed manually by using the software ImageJ. Before performing the actual experiments, it is mandatory to understand and control artefacts that may be induced by the electron beam so that they can be eliminated. The electron beam effects were examined by exposing a nanofiber to a beam current density of 830 e/nm²s in 2 mbar O₂ at room temperature in 1 hour. Under these conditions, the exposed nanofiber reduced its diameter at a rate of ca. 0.5 nm/min. To minimize the beam induced nanofiber shrinkage in the in situ TEM calcination experiment, the low electron beam current density of ca. 800 e/nm²s was used through the entire experiment. The TEM images were acquired every forth minute and the electron beam was removed from the region in the time between image acquisitions. Including time needed for focusing and imaging, the sample regions used in the present analyses were exposed to the electron beam for ca. 40 s per image, giving a total exposure time of ca. 32 min. Based on the measured shrinkage rates, the total shrinkage of the fibers caused by the electron beam can therefore be estimated to 16 nm, which is negligible compared to calcination induced shrinkage (a reduction of several hundreds of nanometers in diameter). It should however be noted that the projected beam induced shrinkage may accelerate as the fiber becomes thinner and that the beam induced shrinkage therefore could be underestimated. However, after the in situ TEM calcination experiment, the regions monitored during the experiment were compared with regions that were previously unexposed to the electron beam. Similar nanofiber structures were found in both types of regions. It is therefore concluded that the influence of the electron beam was not dominating the structural dynamics presented in this study.

2.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed by Netzsch STA 409CD Thermobalance on the electrospun LSC nanofibers, electrospun PVP nanofibers as well as three precursors: $(\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The samples were spread out on the surface of an Al_2O_3 sample holder mounted vertically in the test chamber. The TGA experiments were performed in a flow of 50 Nml/min 0.2 % O_2/N_2 so the oxygen partial pressure used here is identical to that of the in situ TEM experiment. The temperature was ramped from room temperature to 1000°C at 5 °C/min as in the in situ TEM experiment.

3. Results and discussion

3.1 TGA results

The results of the thermogravimetric analysis (TGA) of the electrospun $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_{3-\delta}$ (LSC) nanofibers are presented in Figure 1. Figure 1a reveals a complex mass-temperature dependence of the electrospun nanofibers (red, labelled as LSC Nanofiber) with several temperature intervals of accelerated mass losses. The accelerated mass losses are observed as peaks in the derivative of the mass loss curve (Figure 1b). This complexity could be expected, since the calcination process includes the dehydration of crystal water, the decomposition of three different precursors and in addition the decomposition of PVP. To help in identifying the temperature intervals for the decomposition of each precursor and PVP, Figure 1a also presents results from pure PVP nanofibers (blue), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ powder (orange), $\text{Sr}(\text{NO}_3)_2$ powder (green) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ powder (purple). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are the first precursors to dehydrate and decompose (ca. 30-230°C and 30-600°C, respectively), while $\text{Sr}(\text{NO}_3)_2$ decomposes at higher temperatures (ca. 500-700°C). The decomposition of PVP initiates at ca. 350 °C with an exothermic peak centered at 410 °C (Figure 1b). The mass loss peaks for the LSC nanofiber can be correlated with the mass losses for the individual precursors and for the pure PVP. It is therefore reasonable to assume that the precursors and PVP decompose at the same temperature intervals when mixed in the electrospun nanofibers.

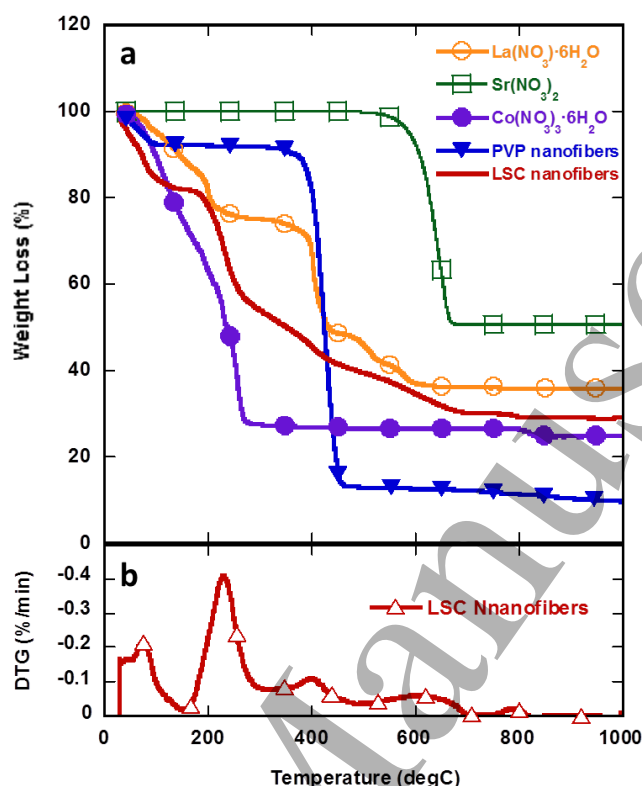


Figure 1: a) The mass loss as a function of temperature of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, PVP nanofibers and LSC nanofibers; b) The derivative mass loss of LSC nanofibers as a function of temperature. During thermogravimetric analysis, all samples were exposed to 0.2 % O_2/N_2 at a constant ramping rate of 5 °C/min.

3.2 In situ TEM imaging

In situ TEM images of the same nanofiber at selected temperatures are presented in Figure 2a-h (A movie of the entire in situ TEM image sequence is available in the Supplementary information). From Figure 2, it can be observed that the fiber diameter is reduced as a function of temperature. In addition, the internal structure of the fiber is changed from an amorphous structure to the appearance of nanograins in the fiber.

To quantify these observations, the diameters of the fiber and of the individual nanograins were measured. Figure 3a presents the diameter of the nanofiber (blue) and the mean diameter of nano-grains in the nanofiber (red) as a function of temperature. When initiating the calcination process, the nanofiber has a diameter of ca. 800 nm (Figure 3a). While ramping the temperature from room temperature (RT) to 330 °C, the diameter decreases to ca. 700 nm (Figure 3a). According to Figure 1, this is mainly due to loss of crystal water and decomposition of $\text{Co}(\text{NO}_3)_3$. At 350 °C, which is the onset temperature for PVP decomposition (Figure 1a), the outer surface of the nanofiber appears corroded (Figure 2c). As the temperature is increased further, the nanofiber diameter is rapidly reduced to ca. 350 nm at 410 °C

(Figure 3a), which is mainly due to PVP decomposition according to Figure 1. At higher temperature, the nanofiber diameter is approximately constant (Figure 3a), despite of the mass losses due to the decomposition of $\text{La}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$ (Figure 1) and the change in nanofiber structure (Figure 2e-h). A small increase in the fiber diameter is, however, observed at ca. 600 °C (Figure 3a), where the $\text{Sr}(\text{NO}_3)_2$ is decomposed with the highest rate (Figure 1).

One type of structural change in the high temperature range is the formation, coarsening and sintering of nano-grains in the nanofiber (Figure 2e-h, Figure 3a). At 510 °C, a mean grain size of ca. 15 nm is observed. When temperature is increased further, the mean grain size of the nanofiber increases (Figure 3a). Smaller grains are expected below 510 °C, but they are too small to be well-defined in the TEM images which represent projections of the nanofiber. Therefore, the exact onset temperature of grain formation cannot be determined from this experiment. To verify the validity of the grain size analysis by in situ TEM, we also carried out grain sizes analysis on nanofibers that were calcined in air in a tube furnace at constant temperatures of 600 °C, 800 °C and 1000 °C for 4 hours (Figure 3a, black X's). It can be seen that the in situ and post mortem grain sizes are consistent.

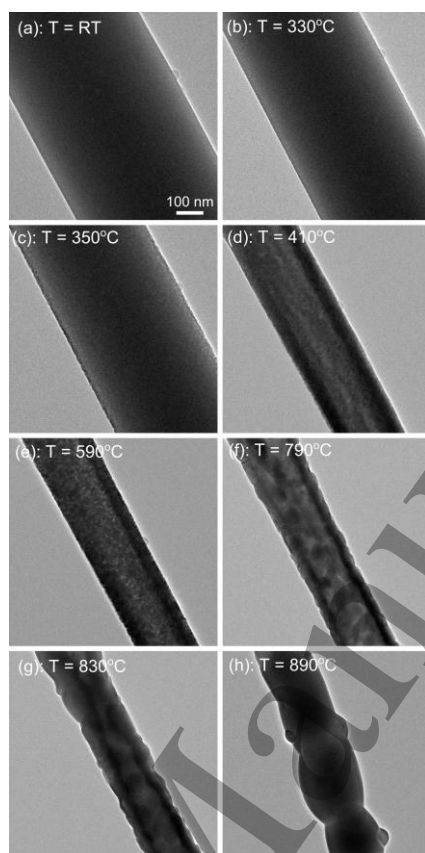


Figure 2: Time-lapsed TEM images recorded in situ on the same nanofiber during exposure to 2 mbar O_2 and at the constant temperature ramping rate of $5^\circ\text{C}/\text{min}$ from room temperature (RT) to 890°C . The images present the fiber at (a) RT, (b) $T = 330^\circ\text{C}$, (c) $T = 350^\circ\text{C}$, (d) $T = 410^\circ\text{C}$, (e) $T = 590^\circ\text{C}$, (f) $T = 790^\circ\text{C}$, (g) $T = 830^\circ\text{C}$ and (h) $T = 890^\circ\text{C}$. The nanofiber contains $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and PVP.

A closer inspection of Figure 2d-f reveals another type of nanofiber structure: there is a strong contrast between the dark edge and the light center of the nanofiber. According to mass-thickness contrast theory, this means that the sample density is lower in the nanofiber center relatively to that near the edges, indicating the nanofiber has a nanotube structure with a low density core. Averaged intensity line profiles across the nanofiber at different temperatures are presented in Figure 3b. For a dense fiber, the intensity profiles will show gradually lower intensity when moving from the edge to the center (See for example the lines for the RT and 250°C in Figure 3b). For temperatures ranging from 370°C to 790°C , it is on the contrary observed that the intensity near the center increases relative to the edges (Figure 3b). This shows that the density of the fibers is lower at the center than near the surface. The observation of an apparent low density core can either be explained a) by the presence of different types of materials, meaning high density materials at the positions near the edges and low density materials at the core, or b) by a void at the core of the fiber – a so-called nanotube. At higher temperatures the low density core disappears, which is clearly observed at 890°C (Figure 3b). The disappearance of the low density core at

the higher temperatures can be explained by the coarsening of nanograins within the fiber. At 830 °C, for example, the mean grain size is ca. 1/3 of the nanofiber diameter (Figure 2g and Figure 3b). At 890 °C, instead of the low density core structure, a so-called nano-pearl string structure with individual particles sizes of ca. 200 nm is observed (Figure 2h). Further increase in temperature resulted in rupture of the nano-pearl string structure into individual nanoparticles.

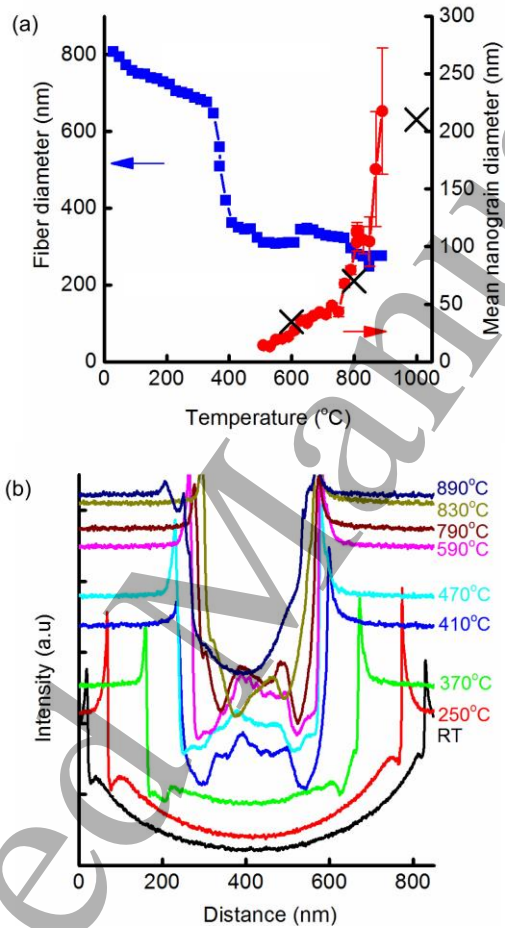


Figure 3: (a) Fiber diameter (line marked by squares) and the mean LSC nanograin diameter (line marked by spheres) as a function of temperature for the fiber in Figure 2. Error bars for the mean LSC nanograin size refer to the standard deviation. Black X is the mean grain sizes of the nanofibers that were calcined in a tube furnace. (b) Intensity line profiles across the fiber in Figure 2 for the indicated temperatures. The line profiles are averaged along the length of the fiber.

3.3 in situ TEM diffraction

Selected area electron diffraction (SAED) was performed on the same LSC nanofiber during the in situ experiment. At 480°C, the broad diffuse signal was observed, which means that the nanofiber has an amorphous structure and that the LSC phase was not yet formed (Figure 4a). Combined with the TEM image information, this indicates that the onset temperature of oxide nano-grain formation is in the

temperature interval of 480-510 °C. This is close to the onset temperature of $\text{Sr}(\text{NO}_3)_2$ decomposition (Figure 1). A ring pattern confirming the presence of nanocrystals is observed at 620 °C (Figure 4b). At higher temperature, the number of diffraction spots decreases so that the ring pattern breaks up (Figure 4b-d). This is consistent with the coarsening of the nanograins with temperature increase. Moreover, the diffraction patterns observed at temperatures from 620 to 890 °C (Figure 4b-d) were found to be consistent with cubic perovskite-type $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. It should be noted that a rhombohedral structure would be expected for LSC at room temperature, and the cubic structure is expected at these elevated temperatures [24].

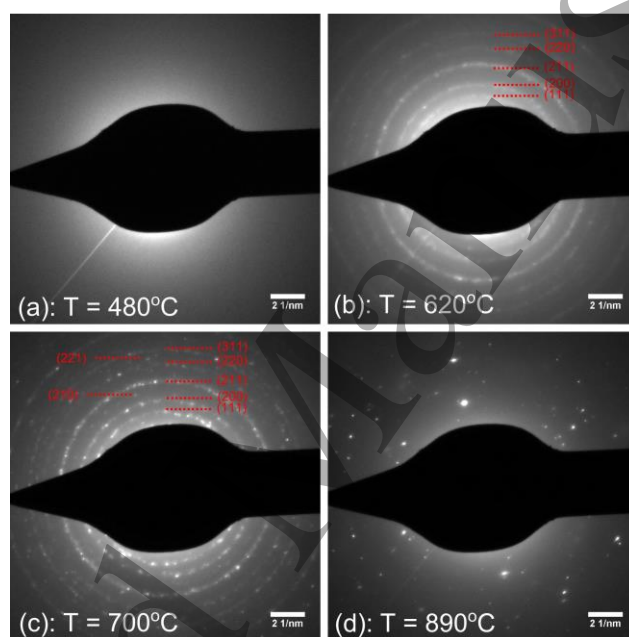


Figure 4: (a-f) Time-lapsed SAED patterns recorded in situ on the same LSC-PVP fiber as presented in Figure 2 during the exposure to 2 mbar O_2 and at the constant temperature ramping rate of 5 °C/min. Miller indices for cubic $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at 900 K [24] is added to (b) and (c) for comparison (red).

Regarding to the low density core structure observed in Figures 2 and 3b, it is interesting that all diffraction ring at the temperatures of 620 °C and 700 °C are consistent with one material, i.e. the cubic perovskite LSC. This observation strongly suggest that the fibers at these temperatures are nanotubes composed of cubic LSC rather than dense fibers composed of different materials with significantly different densities. We can therefore conclude that the in situ TEM experiment shows that three different LSC structures can be obtained by calcination and sintering at specific temperature ranges: nanotubes (ca. 600-800 °C), nanofibers (ca. 800-850 °C) and nano-pearl strings (ca. 850-900 °C).

It is well-known that ABO_3 materials have exhibited unusual properties in varied applications such as solid oxide fuel cells, catalysis, and sensors due to the defective structures and excellent oxygen mobility.

Among those materials, cubic perovskite-type $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3.5}$ is considered as one of the best-performing catalysts due to the enhanced electrocatalytic activity toward oxygen reduction and increased ionic conductivity at intermediate temperature [25-28]. In this experiment, the calcination temperature to obtain cubic structure of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3.5}$ was found to be ca. 620 °C. This temperature is significantly lower than the typical calcination temperatures for conventional methods [29-31], which range from 800 to 1200°C. Therefore, the 1D materials made by our sol-gel assisted electrospinning with lower energy consumption open ways to many applications of metal oxide that required versatile and affordable synthesis methods.

3.4 Fiber structure evolution

Based on the in situ TEM experiments, we can conclude that perovskite LSC nanotubes can be obtained at relatively low temperatures (620 °C to 800 °C). Furthermore, the nanotubes can be obtained alone by controlling the calcination and sintering process rather than using more complex methods such as dual-nozzle electrospinning which is considered to be difficult to scale up for industrial applications. Sintering at slightly higher temperatures (800-850 °C) transformed the nanotube structure into a dense nanofiber. At the high sintering temperature of ca. 890 °C, the nano-pearl string was formed without the rupture of the 1D structure. Nano-pearl strings has previously been used as anode materials for rechargeable lithium batteries to provide high electron transport along the longitudinal direction [12].

It is also important to mention that both temperature and ramping rate are important factors determining the structure of nanofibers during calcination and sintering. Calcination of the same nanofiber at 800 °C for 3 h at higher ramping rate of 15 °C/min did not result in the formation of nanofibers, but a mixture of short nanotubes and broken pieces as shown in Figure S2a in the supplementary information. This indicates that the fibers were broken apart into small pieces during temperature ramping at high rate. This fracture of the fibers into small disconnected pieces suggests that the fibers were torn apart by a rapid process, almost like an explosion.

To the best of our knowledge, the structural evolution of electrospun nanofibers containing precursors and PVP presented in this work has not previously been described or explained. Here we allow ourselves to speculate a possible mechanism for the observed structural evolution: the low density core structure is pronounced immediately after the decomposition of PVP (Figure 3, at 410°C). We emphasize three points: 1) the PVP decomposition produces gases (such as CO, CO₂ and H₂O), 2) the PVP decomposition is a fast process (Figure 1 and Figure 3a) and 3) the fibers appear to fracture rapidly (or explode) at higher ramping rate (Figure S2). This suggests that the PVP decomposition leads to an increase of the internal pressure inside the fiber to form an outward pressure gradient. We therefore suggest a mechanism where the residue of the core is pushed to the surface, driven by the relatively high internal pressure and thereby making a transition from nanofiber to low density core fiber during the shrinkage in diameter due to the

loss of oxidized PVP. Further increase in temperature allows coarsening and sintering of grains on the nanofiber with a slight decrease in nanofiber diameter (as shown in Figure 3b). At the temperature of 800 °C, the low density core structure disappears as a result of continuing growth in grain size to form a dense nanofiber.

The driving forces for the structural evolution are double-folded: 1) the decomposition of polymer that is present in the initial nanofiber, and 2) sintering behaviors of nanograins on the nanofiber. A controlled calcination process can likely be applied in producing other metal oxides in the form of nanofibers, nanotubes and nano-pearl strings. Yet the structural transition temperatures might vary depending on the properties of precursors and carrier polymers.

Preliminary electrochemical tests of the symmetrical cell, composed of a Gadolinium-doped Ceria (CGO) electrolyte and electrodes made of the LSC nanofibers, showed a lower polarization resistance for all temperatures in the temperature range of 500-800°C, as compared to the symmetric cell composed of CGO electrolyte and LSC nanoparticle electrodes (see details in the supplementary information). An additional electrochemical study is in progress to investigate the possible advantages of using LSC fibers as electrodes in fuel and electrolysis cells.

4. Conclusions

The structure evolution of a $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{CoO}_{3-\delta}$ (LSC) nanofiber was determined as a function of temperature in oxygen by in situ TEM. Three distinct 1D geometries were obtained simply as a result of temperature ramping: nanotube (620-800 °C), dense nanofiber (800-850 °C) and nano pearl-string (890 °C). Prior to the in situ TEM calcination and sintering, the fiber was prepared by electrospinning of LSC precursors and PVP and had no internal structures. Above a temperature of 620 °C, the LSC nanotube was composed of cubic perovskite-type nanograins that coarsened and sintered as a function of temperature. The observations show that different metal oxide nanofiber geometries can be obtained by simply controlling the calcination and sintering process of electrospun nanofibers. This represents a facile, inexpensive and up-scalable route to design structured 1D metal oxide nanomaterial.

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